

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

205892US0PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/830566INTERNATIONAL APPLICATION NO.
PCT/EP99/08284INTERNATIONAL FILING DATE
30 October 1999PRIORITY DATE CLAIMED
05 November 1998

TITLE OF INVENTION

AQUEOUS DISPERSIONS OF WATER-SOLUBLE POLYMERS OF N-VINYLCARBOXAMIDES, THEIR PREPARATION AND THEIR USE

APPLICANT(S) FOR DO/EO/US

Anton NEGELE, et al

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☒ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report**Notice of Priority****PCT/IB/304****PCT/IB/308**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.53) 09/830566	INTERNATIONAL APPLICATION NO. PCT/EP99/08284	ATTORNEY'S DOCKET NUMBER 205892US0PCT
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24. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **\$1000.00**
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **\$860.00**
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **\$710.00**
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **\$690.00**
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **\$100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =**\$860.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

\$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	8 - 20 =	0	x \$18.00		\$0.00
Independent claims	2 - 3 =	0	x \$80.00		\$0.00

Multiple Dependent Claims (check if applicable). ☐**\$0.00****TOTAL OF ABOVE CALCULATIONS =****\$860.00**

☐ Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.

\$0.00**SUBTOTAL =****\$860.00**

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

\$0.00**TOTAL NATIONAL FEE =****\$860.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☐

\$0.00**TOTAL FEES ENCLOSED =****\$860.00**

Amount to be: refunded	\$
charged	\$

- a. ☒ A check in the amount of **\$860.00** to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030**. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Surinder Sachar
Registration No. 34,423

**22850**

SIGNATURE

Norman F. Oblon

NAME

24,618

REGISTRATION NUMBER

May 7 2001

DATE

IN RE APPLICATION OF: Anton NEGELE, et al

SERIAL NO.: New U.S. PCT Application (Based on PCT/EP99/08284)

FILED: HERewith

FOR: AQUEOUS DISPERSIONS OF WATER-SOLUBLE POLYMERS OF N-VINYLCARBOXAMIDES, THEIR PREPARATION AND THEIR USE

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

Sir:

Transmitted herewith is an amendment in the above-identified application.

- ☒ No additional fee is required.
- ☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement previously submitted.
- ☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement submitted herewith.
- ☒ Additional documents filed herewith: English Translation, Declaration, Notice of Priority, Check for \$860.00, PCT Transmittal Letter, Preliminary Amendment, PCT/IB/304, PCT/IB/308, International Search Report, Request for Consideration of Documents Cited in International Search Report, Translation of Annexes to the International Preliminary Examination Report, Amended Sheets 15-17.

The fee has been calculated as shown below.

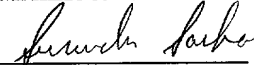
OTHER THAN A

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	CLAIMS REMAINING AFTER		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE	ADDITIONAL FEE		RATE	ADDITIONAL FEE	
TOTAL	* 8	MINUS	** 20	= 0		X9 =	\$		X18 =	\$.00	
INDEP	* 2	MINUS	*** 3	= 0		X40 =	\$		X80 =	\$.00	
<input type="checkbox"/>	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM						+135=	\$		+270=	\$
TOTAL							\$		TOTAL	\$.00	

A check in the amount of \$_____ is attached.

XX Please charge any additional fees for the papers being filed herewith and for which no check is enclosed herewith, or credit any overpayment to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

XX If these papers are not considered timely filed by the Patent and Trademark Office, then a petition is hereby made under 37 C.F.R. §1.136, and any additional fees required under 37 C.F.R. §1.136 for any necessary extension of time may be charged to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.


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*If the entry in Column 2 is less than the entry in Column 1 write "0" in Column 3.
 **If the "Highest Number Previously paid for" IN THIS SPACE is less than 20 write "20" in this space.
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09/830566

JC08 Rec'd PCT/PTO 07 MAY 2009

205892US0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :

ANTON NEGELE ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: NEW US PCT APPLN :
(BASED ON PCT/EP99/08284)

FILED: HERewith :

FOR: AQUEOUS DISPERSIONS OF WATER-
SOLUBLE POLYMERS OF N-
VINYL CARBOXAMIDES, THEIR
PREPARATION AND THEIR USE

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as follows:

3. (Amended) An aqueous dispersion of a water-soluble polymer as claimed in claim 1, wherein the dispersion contains as component (A) a homopolymer of N-vinylformamide.
4. (Amended) An aqueous dispersion of a water-soluble polymer as claimed in claim 1, wherein the N-vinylformamide units and/or vinylacetamide units of the polymer (A) have

been partially or completely converted into a polymer containing vinylamine units by hydrolysis with acids or bases.

7. (Amended) A process as claimed in claim 5, wherein the polymeric dispersants (B) used are polyethylene glycol, polypropylene glycol, copolymers of ethylene glycol and propylene glycol, polyvinyl acetate, polyvinyl alcohol, polyvinylpyridine, polyvinylimidazole, polyvinylsuccinimide, polydiallyldimethylammonium chloride, polyethyleneimine and mixtures thereof.

8. (Amended) A process as claimed in claim 5, wherein

(A) N-vinylformamide, if desired together with other monoethylenically unsaturated monomers, and

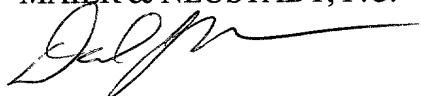
(B) polyethylene glycol, polyvinylpyrrolidone or mixtures thereof are polymerized at from 40 to 55°C with water-soluble azo initiators.

REMARKS

Claims 1-8 are active in the present application. The claims are amended to remove multiple dependencies. No new matter is added. An action on the merits and allowance of the claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
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Marked-Up Copy

Serial No: _____

Amendment Filed on: _____

IN THE CLAIMS

--3. (Amended) An aqueous dispersion of a water-soluble polymer as claimed in claim 1 [or 2], wherein the dispersion contains as component (A) a homopolymer of N-vinylformamide.

4. (Amended) An aqueous dispersion of a water-soluble polymer as claimed in claim 1 [or 2], wherein the N-vinylformamide units and/or vinylacetamide units of the polymer (A) have been partially or completely converted into a polymer containing vinylamine units by hydrolysis with acids or bases.

7. (Amended) A process as claimed in claim 5 [or 6], wherein the polymeric dispersants (B) used are polyethylene glycol, polypropylene glycol, copolymers of ethylene glycol and propylene glycol, polyvinyl acetate, polyvinyl alcohol, polyvinylpyridine, polyvinylimidazole, polyvinylsuccinimide, polydiallyldimethylammonium chloride, polyethyleneimine and mixtures thereof.

8. (Amended) A process as claimed in [any of claims 5 to 7] claim 5, wherein (A) N-vinylformamide, if desired together with other monoethylenically unsaturated monomers, and

(B) polyethylene glycol, polyvinylpyrrolidone or mixtures thereof

are polymerized at from 40 to 55°C with water-soluble azo initiators.--

Aqueous dispersions of water-soluble polymers of
N-vinylcarboxamides, their preparation and their use

- 5 The present invention relates to aqueous dispersions of
water-soluble polymers of N-vinylcarboxamides, processes for
their preparation and their use in papermaking.

- EP-A-01 83 466 discloses a process for the preparation of aqueous
10 dispersions of water-soluble polymers, cationic monomers, for
example dialkylaminoacrylamides quaternized with benzyl chloride,
being polymerized in an aqueous salt solution in the presence of
a polymeric dispersant. Dispersants used are, for example,
polyols, polyalkylene ethers, alkali metal salts of polyacrylic
15 acid and alkali metal salts of poly-2-acrylamido-2-methylpropane-
sulfonic acid. Salt concentration in the polymerization medium is
preferably from 15% by weight to the saturation limit.

- DE-A-44 30 069 discloses aqueous, solvent-free dispersions of
20 cationic polymers, which are used as sizes for paper. The
polymers are prepared by free radical polymerization of cationic
monomers, if desired as a mixture with other monomers in solution
or dispersion or by mass polymerization.

- 25 DE-A 195 32 229 discloses a process for the preparation of
low-viscosity, water-soluble polymer dispersions. In this
process, water-soluble monomers, as a mixture with a
crosslinkable N-methylol compound, or polymerized in aqueous
solution in the presence of at least one polymeric dispersant,
30 the resulting polymer being incompatible with the dispersant. The
dispersions thus obtained are used as flocculants.

- WO-A-97/30094 discloses a process for the preparation of
dispersions of water-soluble cationic vinyl polymers,
35 water-soluble, cationic hydrophobically modified vinyl monomers
or water-soluble, nonionic, hydrophobic vinyl monomers being
polymerized with water-soluble, cationic and/or water-soluble
neutral vinyl monomers in aqueous salt solutions using a
water-soluble initiator in the presence of stabilizers which
40 consist of a graft copolymer which contains polyethylene oxide as
the grafting base and grafted-on cationic vinyl monomers as side
chains. WO-A 97/34933 relates to aqueous dispersions of high
molecular weight, nonionic or anionic polymers which were
prepared by polymerization of the monomers in a saturated salt
45 solution with addition of an anionic, water-soluble polymer

stabilizer. Preferably used monomers are acrylamide and acrylic acid.

It is an object of the present invention to provide aqueous
5 dispersions of water-soluble polymers, which dispersions are
virtually free of stabilizing inorganic salts.

We have found that this object is achieved, according to the
invention, by aqueous dispersions of water-soluble polymers of
10 N-vinylformamide and/or of N-vinylacetamide if the dispersions
contain, based on 100 parts by weight of water,

(A) from 5 to 80 parts by weight of a water-soluble polymer
containing N-vinylformamide units and/or N-vinylacetamide
15 units and having particle sizes of from 50 nm to 2 μ m and

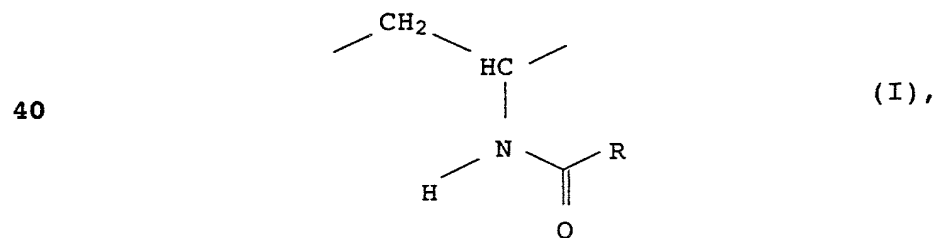
(B) from 1 to 50 parts by weight of at least one polymeric
dispersant which is incompatible with the water-soluble
20 polymers (A) in aqueous solution.

The aqueous dispersions of water-soluble polymers preferably
contain, based on 100 parts by weight of water,

(A) from 10 to 50 parts by weight of a water-soluble polymer
25 containing N-vinylformamide units and/or N-vinylacetamide
units and

(B) from 5 to 40 parts by weight of at least one polymeric
dispersant which is incompatible with the water-soluble
30 polymers (A) in aqueous solution.

Particularly preferred dispersions are those which contain, as
component (A), homopolymers of N-vinylformamide. N-vinylformamide
units and N-vinylacetamide units can be characterized with the
35 aid of the following formula:



45 where R is H or CH₃.

The water-soluble polymers containing N-vinylformamide units and/or N-vinylacetamide units can, if required, contain from 1 to 80, preferably from 5 to 30, % by weight of further monomers as copolymerized units. Such monomers are, for example,

- 5 monoethylenically unsaturated carboxylic acids of 3 to 8 carbon atoms, such as acrylic acid, methacrylic acid, dimethacrylic acid, ethacrylic acid, maleic acid, citraconic acid, methylenemalononic acid, allylacetic acid, vinylacetic acid, crotonic acid, fumaric acid, mesaconic acid and itaconic acid.
- 10 From this group of monomers, acrylic acid, methacrylic acid, maleic acid or mixtures of said carboxylic acids are preferably used. The monoethylenically unsaturated carboxylic acids are used either in the form of the free acids or in the form of their free alkali metal, alkaline earth metal or ammonium salts in the
- 15 copolymerization. For neutralization of the free carboxylic acids, sodium hydroxide solution, potassium hydroxide solution, sodium carbonate, potassium carbonate, sodium bicarbonate, magnesium oxide, calcium hydroxide, calcium oxide, gaseous or aqueous ammonia, triethylamine, ethanolamine, diethanolamine,
- 20 triethanolamine, morpholine, diethylenetriamine or tetraethylenepentamine is preferably used.

Further suitable monomers are, for example, the esters, amides and nitriles of the abovementioned carboxylic acids, e.g. methyl

- 25 acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxyisobutyl acrylate, hydroxyisobutyl methacrylate, monomethyl maleate, dimethyl maleate, monoethyl
- 30 maleate, diethyl maleate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, acrylamide, methacrylamide, N-dimethylacrylamide, N-tert-butylacrylamide, acrylonitrile, methacrylonitrile, dimethylaminoethyl acrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate and the salts of the
- 35 last-mentioned basic monomers with carboxylic acids or mineral acids and the quaternized products of the basic (meth)acrylates.

Other suitable copolymerizable monomers are furthermore acrylamidoglycolic acid, vinylsulfonic acid, allylsulfonic acid,

- 40 methallylsulfonic acid, styrenesulfonic acid, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate and acrylamidomethylpropanesulfonic acid and monomers containing phosphoric acid groups, such as vinylphosphonic acid, allylphosphonic acid and acrylamidomethylpropanephosphonic acid.

- 45 The monomers containing acid groups can be used in the

polymerization in the form of free acid groups and in a form partially or completely neutralized with bases.

Further suitable copolymerizable compounds are

- 5 N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, N-vinyl-2-methylimidazole, N-vinyl-4-methylimidazole, diallylammonium chloride, vinyl acetate, vinyl propionate and styrene. It is of course also possible to use mixtures of said monomers. The said monomers when polymerized alone do not give
- 10 water-soluble polymers, the polymers containing N-vinylformamide units and/or N-vinylacetamide units contain these comonomers as polymerized units only in amounts such that the copolymers are still water-soluble. In contrast to water-in-oil polymer emulsions, no organic solvents are required for the novel aqueous
- 15 dispersions. As is evident from the prior art stated at the outset, concentrated solutions of inorganic salts are a conventional medium for the preparation of aqueous dispersions of water-soluble polymers. As a result, the known dispersions have a very high salt load. Novel aqueous dispersions of water-soluble
- 20 polymers are in comparison virtually salt-free. The aqueous dispersions of water-soluble polymers of N-vinylformamide and/or N-vinylacetamide preferably have a high polymer content and preferably contain polymers having high molar masses in combination with low viscosity. The molar masses of the polymers
- 25 containing N-vinylformamide units and/or N-vinylacetamide units are, for example, from $5 \cdot 10^4$ to $1 \cdot 10^7$, preferably from $2 \cdot 10^5$ to $1 \cdot 10^6$.

- The polymeric dispersants additionally contained as component (B)
- 30 in the aqueous dispersions differ in the composition from the water-soluble polymers (A) described above. The polymeric dispersant (B) is incompatible with the water-soluble polymer (A). The average molar masses of the polymeric dispersants are preferably from 1000 to 500,000, in particular from 1500 to
- 35 50,000.

- The polymeric dispersant containing at least one functional group selected from ether, hydroxyl, carboxyl, sulfone, sulfate ester, amino, imino, tert-amino and/or quaternary ammonium groups.
- 40 Examples of such compounds are: carboxymethylcellulose, water-soluble starch and starch derivatives, starch esters, starch xanthogenates, starch acetates, dextran, polyalkylene glycols, polyvinyl acetate, polyvinyl alcohol, polyvinylpyrrolidone, polyvinylpyridine, polyethyleneimine,
- 45 polyvinylimidazole, polyvinylsuccinimide and polydiallyldimethylammonium chloride.

5

If the aqueous dispersions of water-soluble polymers of N-vinylcarboxamides are used in papermaking, polymeric dispersants which have further process- or product-improving properties are preferably used for the preparation of these
5 dispersions. In this way, it is possible to offer combination solutions to the papermaker. For example, the dispersants (B) of the aqueous dispersions of water-soluble polymers of N-vinylcarboxamides can be selected from compounds which are employed in papermaking as fixing compositions, wet or dry
10 strength agents, dispersants for inorganic solids, antiadhesion compositions for better release from rollers or detackifiers, with the result that the soft, tacky impurities of the paper stock are converted into brittle deposits. In papermaking, it is of course possible to use further process assistants together
15 with the novel aqueous dispersions. For example, a polyacrylamide or polyethylene oxide having retention activity may additionally be used with a novel aqueous dispersion of poly-N-vinylformamide.

The aqueous dispersions contain from 1 to 50, preferably from 5
20 to 40, parts by weight, based on 100 parts by weight of water, or at least one of the abovementioned polymeric dispersants (B).

The present invention also relates to a process for the preparation of aqueous dispersions of water-soluble polymers of
25 N-vinylformamide and/or of N-vinylacetamide, wherein

(A) from 5 to 80 parts by weight of N-vinylformamide and/or N-vinylacetamide, if desired together with other monoethylenically unsaturated monomers which form
30 water-soluble polymers therewith, and

(B) from 1 to 50 parts by weight of at least one polymeric dispersant which is incompatible with the polymers, formed from the monomers (A), in aqueous solution,
35

in 100 parts by weight of water, are subjected to free radical polymerization at from 30 to 95°C in the presence of from 0.001 to 5.0% by weight, based on the monomers used, of polymerization
40 initiators which form free radicals under the polymerization conditions.

In the preferred embodiment of the process,

- (A) from 10 to 50 parts by weight of N-vinylformamide and/or N-vinylacetamide, if desired together with other monoethylenically unsaturated monomers which form water-soluble polymers therewith, and
- 5 (B) from 5 to 40 parts by weight of at least one polymeric dispersant which is incompatible with the polymers, formed from the monomers (A), in aqueous solution,
- 10 in 100 parts by weight of water, are polymerized at from 40 to 70°C with from 0.5 to 2.0% by weight, based on the monomers used in the polymerization, of the azocompounds which decompose into free radicals under the polymerization conditions.
- 15 The monomers are subjected to free radical polymerization according to the invention, i.e. polymerization inhibitors which form free radicals under the polymerization conditions are used. Suitable compounds of this type are, for example, hydrogen peroxide, peroxides, hydroperoxides, redox catalysts and
- 20 nonoxidizing initiators, such as azocompounds which decompose into free radicals under the polymerization conditions. Such azocompounds are, for example, 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride, 2,2'-azobis(2,4-dimethylvaleronitrile),
- 25 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] or 2,2'-azobisisobutyronitrile. It is of course also possible to use mixtures of different initiators. A particularly preferred preparation process for the aqueous dispersions of water-soluble polymers is one in which
- 30 (A) N-vinylformamide, if desired together with other monoethylenically unsaturated monomers, and
- (B) polyethylene glycol, polyvinylpyrrolidone or mixtures thereof
- 35 are polymerized at from 40 to 55°C with water-soluble azoinitiators. Suitable polymeric dispersants (B) are preferably polyethylene glycol, polypropylene glycol, copolymers of ethylene glycol and propylene glycol, polyvinyl acetate, polyvinyl
- 40 alcohol, polyvinylpyridine, polyvinylimidazole, polyvinylsuccinimide, polydiallyldimethylammonium chloride, polyethyleneimine and mixtures thereof. The molar masses of these polymers are preferably from 1500 to 50,000.
- 45 If polymer dispersions and polymers having low molecular weights are desired, it is possible, for example, to increase the amounts of initiator which are usually used in the polymerization so that

- it is also possible to use amounts of initiator which are outside the abovementioned range for the amounts of initiator. Aqueous dispersions of low molecular weight homo- and copolymers of the suitable vinylcarboxamides can also be obtained by carrying out
- 5 the polymerization in the presence of polymerization regulators and, if required, simultaneously using a larger amount of initiator than that usually required. Suitable polymerization regulators are, for example, compounds containing sulfur in bound form, such as dodecyl mercaptan, thioglycolic acid, thioacetic
- 10 acid and mercaptoalcohols, such as mercaptoethanol, mercaptopropanols and mercaptobutanols. In addition, formic acid, isopropanol and hydrazine in the form of salts with strong acid may also be used as polymerization regulators.
- 15 The molecular weights of the polymers present in dispersed form can also be characterized with the aid of the K values according to Fikentscher. The K values are up to 300 and preferably in the range from 130 to 180. From light scattering experiments, it follows that a K value of 250 corresponds to an average molecular
- 20 weight of the polymers of about 7,000,000 dalton.

- By eliminating formyl groups from polymers containing N-vinylformamide units and by eliminating the group $\text{CH}_3\text{-CO-}$ from polymers containing N-vinylacetamide units, polymers containing
- 25 vinylamine units are formed in each case. Elimination may be effected partially or completely. If the hydrolysis is carried out in the presence of acids, the vinylamine units of the polymers are present as ammonium salts. The hydrolysis can also be carried out with the aid of bases, for example of metal hydroxides, in
- 30 particular of alkali metal and alkaline earth metal hydroxides. Preferably, sodium hydroxide or potassium hydroxide is used. In particular cases, hydrolysis can also be carried out with the aid of ammonia or amines. In the case of the hydrolysis in the presence of bases, the vinylamine units are present in the form
- 35 of free bases.

- Suitable hydrolysis agents are preferably mineral acids, such as halogen halides, which may be used in gaseous form or as an aqueous solution. Concentrated hydrochloric acid, sulfuric acid,
- 40 nitric acid or phosphoric acid and organic acids, such as $\text{C}_1\text{-}$ to $\text{C}_5\text{-}$ carboxylic acids, and aliphatic or aromatic sulfonic acid are preferably used. For example, from 0.05 to 2, in particular from 1 to 1.5, molar equivalents of acid are required per equivalent of formyl groups in the polymers containing polymerized
- 45 N-vinylformamide units. Hydrolysis of the N-vinylformamide units takes place significantly more rapidly than that of the polymers having N-vinylacetamide units. If copolymers of the suitable

vinylcarboxamides with other comonomers are subjected to the hydrolysis, the comonomer units contained in the copolymer can also be chemically modified. For example, vinyl alcohol units are formed from vinyl acetate units. In hydrolysis, acrylic acid units are formed from methyl acrylate units, and acrylamide or acrylic acid units are formed from acrylonitrile units. The hydrolysis of the N-vinylformamide units and/or vinylacetamide units of the polymers (A) can be carried out to an extent of from 5 to 100%, preferably from 10 to 40%. Although aqueous dispersions of water-soluble N-vinylcarboxamides dissolve on dilution with water, the dispersion is surprisingly not destroyed during hydrolysis. The particle diameter of the hydrolyzed particles before and after the hydrolysis is from 50 nm to 2 μ m or preferably from 50 nm to 2 μ m and in most cases from 100 to 700 nm.

The dispersions described above, i.e. the unhydrolyzed as well as the hydrolyzed aqueous dispersions of water-soluble N-vinylcarboxamides, are used as drainage aids, flocculants and retention aids and as wet and dry strength agents and as fixing compositions in papermaking. The cationic polymers can moreover be used as flocculants for wastewaters in the dewatering of sewage sludge, as flocculants in ore dressing and in tertiary oil production or as dispersants, for example, for inorganic and organic pigments, dyes, cement or crop protection agents. The unhydrolyzed as well as the hydrolyzed aqueous dispersions can moreover be used as strength agents for paper, as fixing compositions for soluble and insoluble interfering substances in papermaking and as compositions for paper coating. They can furthermore be used as coating material for fertilizers and crop protection agents and as floorcare compositions. Said aqueous hydrolyzed and unhydrolyzed polymer dispersions can also be used in cosmetics, for example for hair formulations, for example conditioners, hairsetting compositions or conditioners for skincare compositions and as thickeners for cosmetic formulations and furthermore as a component of cosmetic formulations for oral hygiene.

The K values were determined according to H. Fikentscher, Cellulose-Chemie, 13 (1932), 58-64 and 71-74, in aqueous solution at 25°C and at a concentration which, depending on the K value range, of from 0.1 to 5% by weight. The viscosity of the dispersion was measured in each case in a Brookfield viscometer using a no. 4 spindle at 20 rpm and at 20°C. The data in % are percentages by weight.

Example 1

800 g of water, 5 g of sodium dihydrogen phosphate dihydrate, 150 g of polyvinylpyrrolidone (K value 30, determined in 1% strength aqueous solution) and 150 g of polyethylene glycol having a molar mass of 1500 were weighed into a 2 l glass vessel equipped with an anchor stirrer, nitrogen supply line, distillation bridge and reduced pressure regulating means were all processed by stirring to give a homogeneous solution. 500 g of N-vinylformamide were added and the pH of the solution was then brought to 6.5 by adding 25% strength aqueous sodium hydroxide solution. Nitrogen was passed continuously through the reaction mixture, and a solution of 2.5 g of 2,2'-azobis-(2-aminopropane) dihydrochloride in 100 g of water was added and the reaction mixture was heated to 50°C for polymerization. The polymerization was carried out at this temperature and 130 mbar, the resulting heat of polymerization being removed by evaporative cooling. The polymerization time was 13 hours. Within this time, water was distilled off in an amount such that an aqueous dispersion having a solids content of 44% was obtained. It had a viscosity of 15600 mPas, a K value of 140 (measured as 0.1% strength solution in 5% strength aqueous NaCl solution) and a residual N-vinylformamide monomer content of 0.1%.

25 Example 2

1200 g of water, 5 g of sodium dihydrogen phosphate dihydrate, 150 g of polyvinylpyrrolidone (K value 30, determined in 1% strength aqueous solution) and 150 g of polyethylene glycol having a molar mass of 1500 were initially taken in a 2 l glass vessel equipped with an anchor stirrer, nitrogen supply line, distillation bridge and reduced pressure regulating means. The mixture was stirred, and 643 g of N-vinylformamide were added. The pH of the reaction mixture was brought to 6.5 by adding 25% strength aqueous sodium hydroxide solution. Nitrogen was passed continuously through the reaction mixture and 2.5 g of 2,2'-azobis(2-aminopropane) dihydrochloride in the form of a solution in 100 g of water were added and the batch was heated to a polymerization temperature of 50°C. The polymerization was carried out at 130 mbar, the resulting heat of polymerization being removed in the course of 13 hours by evaporative cooling and water being distilled off from the reaction mixture in an amount such that an aqueous dispersion having a solids content of 44.1% and a polyvinylformamide fraction of 25% was obtained. The viscosity of the aqueous dispersion was 5800 mPas. The K value of

the polymer was 148 and the residual N-vinylformamide monomer content was 0.2%.

Example 3

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In the apparatus described in Example 1, first a solution of 1200 g of water, 5 g of sodium dihydrogen phosphate dihydrate, 150 g of polyvinylpyrrolidone (K value 30, measured in 1% strength aqueous solution) and 150 g of polyethylene glycol
10 having a molar mass of 1500 was prepared, and then 500 g of N-vinylformamide were added and a 25% strength aqueous sodium hydroxide solution was added in an amount such that the pH of the solution was 6.5. Nitrogen was passed continuously through the solution, and an aqueous solution of 2.5 g of 2,2'-azobis-
15 (2-aminopropane) dihydrochloride in 100 g of water was added and the mixture was heated to 50°C. The polymerization was carried out at 130 mbar in the course of 13 hours, water being distilled off for evaporative cooling in an amount such that an aqueous polymer dispersion having a solids content of 41.0% was obtained. The
20 viscosity of the dispersion was 3075 mPa.s. The proportion of dispersed polyvinylformamide was 20%. The polymer had a K value (measured as 0.1% strength solution in 5% strength aqueous NaCl solution) of 138 and a residual monomer content of 0.2%.

25 Example 4

In the apparatus stated in Example 1, the solution of 1044 g of water, 5 g of sodium dihydrogen phosphate dihydrate, 200 g of a partially hydrolyzed polyvinyl acetate having a degree of
30 hydrolysis of 86% and 100 g of polyethylene glycol having a molar mass of 1500 was prepared and 500 g of N-vinylformamide were added while stirring. The 25% strength aqueous sodium hydroxide solution was then added in an amount such that the pH was 6.5. Nitrogen was passed through the reaction mixture, and a solution
35 of 2.5 g of 2,2'-azobis(2-aminopropane) dihydrochloride, dissolved in 1000 g of water, was added and the reaction mixture was heated to a polymerization temperature of 50°C. The polymerization was carried out at 130 mbar over a period of 13 hours and with removal of the heat of polymerization by
40 evaporative cooling. Water was distilled off in an amount such that an aqueous dispersion having a solids content of 36% was obtained. The polymer had a K value (measured at a polymer concentration of 0.1% in 5% strength aqueous NaCl solution) of 130 and a residual monomer content of 0.1%. The particle diameter
45 of the dispersed particles was 200 nm.

Example 5

In the apparatus stated in Example 1, first an aqueous solution was prepared by initially taking therein 836 g of water, 5 g of sodium dihydrogen phosphate dihydrate, 150 g of a copolymer of N-vinylcaprolactam and N-vinylmethylacetamide in a molar ratio of 1:1, having a molar mass of 45,000, and 150 g of polyethylene glycol having a molar mass of 1500, adding 500 g of N-vinylformamide while stirring and bringing the pH of the solution to 6.5 by adding 25% strength aqueous sodium hydroxide solution. Nitrogen was then passed continuously through the mixture, a solution of 2.5 g of 2,2'-azobis(2-aminopropane) dihydrochloride in 100 g of water was added and the mixture was heated to 50°C, at which the polymerization was carried out. At the same time, a pressure of 130 mbar was established, and the resulting heat of polymerization was removed by rapid cooling. For this purpose, water was distilled off over a period of 13 hours in an amount such that an aqueous polymer dispersion having a solids content of 43% was formed. The polyvinylformamide content was 26.9%. The aqueous solution had a viscosity of 8700 mPa.s. The polymer had a K value (measured in 5% strength aqueous NaCl solution at a polymer concentration of 0.1%) of 110.2 and a residual N-vinylformamide monomer content of 0.2%. The particle size of the dispersed particles was 200 nm.

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Example 6

216.7 g of the aqueous polymer dispersion prepared according to Example 1 were initially taken in a 3-necked flask which had a capacity of 250 ml and was equipped with a gas inlet tube, reflux condenser and stirrer. 4 g of gaseous hydrogen chloride were passed in while stirring in the course of 10 minutes. The reaction mixture was heated to 50°C and stirred for 5 hours at this temperature. Thereafter, the degree of hydrolysis for the polymer was 10.1%, i.e. the polymer contained 10.1% of vinylamine units. The reaction mixture was neutralized by passing in 2.2 g of ammonia gas. The pH was 7.5. The dispersion had a viscosity of 16,600 mPa.s. The mean particle size of the dispersed particles was 250 nm. The polymer had a molar mass of 900,000 daltons.

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Example 7

206 g of the aqueous dispersion prepared according to Example 3 were initially taken in a 3-necked flask having a capacity of 250 ml and equipped with a gas inlet tube, reflux condenser and stirrer. 20.3 g of hydrogen chloride gas were then passed in while stirring in the course of 25 minutes. The reaction mixture

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was heated to 75°C and then stirred for 2 hours at this temperature. The degree of hydrolysis of the poly-N-vinylformamide was 75%. The dispersion had a viscosity of 7040 mPa.s. The particle size of the dispersion was 300 nm. The 5 molar mass of the polymer was 500,000 daltons.

Example 8

212 g of the dispersion obtained according to Example 3 were initially taken in a 3-necked flask having a capacity of 250 ml. 2.8 g of gaseous hydrogen chloride were then passed in while stirring, and the reaction mixture was heated to 50°C. The mixture was then stirred for 6.5 hours at this temperature. Thereafter, the degree of hydrolysis of the polymer was 8.5%. The aqueous dispersion had a viscosity of 4800 mPa.s. The particle size of the dispersed particles was 200 nm. The polymer had a molar mass of $1.2 \cdot 10^6$ daltons.

Example 9

217.8 g of the polymer dispersion prepared according to Example 3 were initially taken in a 3-necked flask having a capacity of 250 ml. 8 g of gaseous hydrogen chloride were then passed in while stirring, and the reaction mixture was heated to 50°C. The mixture was then stirred for 7 hours at this temperature. Thereafter, the degree of hydrolysis of the polymer was 27.4%. The aqueous dispersion had a viscosity of 4950 mPa.s. The particle size of the dispersed particles was 370 nm and the molar mass was $1.07 \cdot 10^6$ daltons.

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Use examples

Determination of the drainage time

The drainage term was determined in a Schopper-Riegler-tester by draining therein 1 l of the fibrous stock suspension to be tested and in each case determining the drainage time after the passage of 700 ml of water.

Optical transmittance of the white water

The optical transmittance of the white water is a measure of retention of crills and fillers. It was determined with the aid of a photometer and stated in percent. The higher the value for the optical transmittance, the better is the retention. The following starting materials were used:

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The polymers I and II served for comparison with the prior art.

Polymer I:

- Polyamidoamine obtained from adipic acid and diethylenetriamine grafted with ethyleneamine and crosslinked with an
- 5 α,ω -dichloropolyethylene glycol ether (cationic drainage aid and retention aid according to US-A 4 144 123).

Polymer II:

- 10 Commercial cationic copolymer of 70% acrylamide and 30% of dimethylaminoethyl acrylate chloride, K value of the copolymer 250.

Polymer III:

- 15 Commercial cationic polyacrylamide (Praesterat® K 350)

Polymers to be used according to the invention:

20 Polymer IV:

Aqueous dispersion which was obtained according to Example 8 (copolymer of 91.5% of N-vinylformamide units and 8.5% of vinylamine units).

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Example 10

- A pulp having a consistency of 2 g/l was prepared from deinked wastepaper, and 0.2 g/l of china clay was additionally added to
- 30 the stock. The paper stock had a pH of 7. First the drainage rate and then the optical transmittance of the white water were determined. Zero value of the drainage time was 79 seconds. The polymers stated in Tables 1 and 2 were then added in amounts of 0.02, 0.04 and 0.08%, based on dry fiber, to the fiber suspension
- 35 and the drainage times and the optical transmittance of the white waters were determined. The results shown in Tables 1 and 2 were determined.

Drainage time [s]

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	Addition [%] 0.02	of the polymer 0.04	to the paper stock 0.08
Polymer I	55	40	28
45 Polymer II	33	25	18
Polymer III	43	32	23
Polymer IV	39	30	23

Optical transmittance [%]

5		Addition [%] 0.02	of the polymer 0.04	to the paper stock 0.08
	Polymer I	51	63	77
	Polymer II	73	86	93
	Polymer III	62	75	86
10	Polymer IV	67	74	83

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We claim:-

1. An aqueous dispersion of a water-soluble polymer of
5 N-vinylformamide and/or of N-vinylacetamide, wherein the dispersion contains, based on 100 parts by weight of water,
 - (A) from 5 to 80 parts by weight of a water-soluble polymer
10 containing N-vinylformamide units and/or N-vinylacetamide units and having a particle size of from 50 nm to 2 μ m
 - (B) from 1 to 50 parts by weight of at least one polymeric
15 dispersant which is selected from the group consisting of carboxymethylcellulose, water-soluble starch, starch esters, starch xanthogenates, starch acetates, dextran, polyalkylene glycols, polyvinyl acetate, polyvinyl
20 alcohol, polyvinylpyrrolidone, polyvinylpyridine, polyethyleneimine, polyvinylimidazole, polyvinylsuccinimide and polydiallyldimethylammonium chloride.
2. An aqueous dispersion of a water-soluble polymer as claimed
25 in claim 1, wherein the dispersion contains, based on 100 parts by weight of water,
 - (A) from 10 to 50 parts by weight of a water-soluble polymer
containing N-vinylformamide units and/or N-vinylacetamide
units and
 - 30 (B) from 5 to 40 parts by weight of at least one polymeric dispersant.
3. An aqueous dispersion of a water-soluble polymer as claimed
35 in claim 1 or 2, wherein the dispersion contains as component (A) a homopolymer of N-vinylformamide.
4. An aqueous dispersion of a water-soluble polymer as claimed
40 in claim 1 or 2, wherein the N-vinylformamide units and/or vinylacetamide units of the polymer (A) have been partially or completely converted into a polymer containing vinylamine units by hydrolysis with acids or bases.
5. A process for the preparation of aqueous dispersions of
45 water-soluble polymers of N-vinylformamide and/or of N-vinylacetamide, wherein

(A) from 5 to 80 parts by weight of N-vinylformamide and/or N-vinylacetamide, if desired together with other monoethylenically unsaturated monomers, which form water-soluble polymers therewith, and

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(B) from 1 to 50 parts by weight of at least one polymeric dispersant which is selected from the group comprising carboxymethylcellulose, water-soluble starch, starch esters, starch xanthogenates, starch acetates, dextran, polyalkylene glycols, polyvinyl acetate, polyvinyl alcohol, polyvinylpyrrolidone, polyvinylpyridine, polyethyleneimine, polyvinylimidazole, polyvinylsuccinimide and polydiallyldimethylammonium chloride,

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in 100 parts by weight of water, are subjected to free radical polymerization at from 30 to 95°C in the presence of from 0.001 to 5.0% by weight, based on the monomers used, of polymerization initiators which form free radicals under the polymerization conditions.

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6. A process as claimed in claim 5, wherein

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(A) from 10 to 50 parts by weight of N-vinylformamide and/or vinylacetamide, if desired together with other monoethylenically unsaturated monomers which form water-soluble polymers therewith, and

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(B) from 5 to 40 parts by weight of at least one polymeric dispersant.

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in 100 parts by weight of water, are polymerized at from 40 to 70°C with from 0.5 to 2.0% by weight, based on the monomers used in the polymerization, of azocompounds which decompose into free radicals under the polymerization conditions.

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7. A process as claimed in claim 5 or 6, wherein the polymeric dispersants (B) used are polyethylene glycol, polypropylene glycol, copolymers of ethylene glycol and propylene glycol, polyvinyl acetate, polyvinyl alcohol, polyvinylpyridine, polyvinylimidazole, polyvinylsuccinimide, polydiallyldimethylammonium chloride, polyethyleneimine and mixtures thereof.

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8. A process as claimed in any of claims 5 to 7, wherein

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AMENDED SHEET

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- (A) N-vinylformamide, if desired together with other monoethylenically unsaturated monomers, and
- (B) polyethylene glycol, polyvinylpyrrolidone or mixtures thereof

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are polymerized at from 40 to 55°C with water-soluble azo initiators.

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Aqueous dispersions of water-soluble polymers of
N-vinylcarboxamides, their preparation and their use

5 Abstract

Aqueous dispersions of water-soluble polymers of
N-vinylcarboxamides contain, based on 100 parts of water,

- 10 (A) from 5 to 80 parts by weight of water-soluble polymer
containing N-vinylformamide units and/or N-vinylacetamide units
and having particle sizes of from 50 nm to 2 μ m and
- (B) from 1 to 50 parts by weight of at least one polymeric
15 dispersant which is incompatible with the water-soluble polymers
(A) in aqueous solution, which dispersions are prepared by
polymerizing
- (A) from 5 to 80 parts by weight of N-vinylformamide and/or
20 N-vinylacetamide, if desired together with other
monoethylenically unsaturated monomers which form
water-soluble polymers therewith, and
- (B) from 1 to 50 parts by weight of at least one polymeric
25 dispersant which is incompatible with the polymers, formed
from the monomers (A), in aqueous solution,
- in 100 parts by weight of water, at from 30 to 95°C in the
presence of from 0.001 to 5.0% by weight, based on the monomers
30 used, and the aqueous dispersions of water-soluble polymers are
used as drainage aids, flocculants and retention aids and as wet
and dry strength agents and as fixing compositions in
papermaking.

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Declaration, Power of Attorney

Page 1 of 4

0050/049505

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Aqueous dispersions of water-soluble polymers of N-vinylcarboxamides,
their preparation and their use

the specification of which

☐ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and amended on _____.

☒ was filed as PCT international application

Number PCT/EP99/08284

on October 30, 1999

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)–(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19851024.1	Germany	05 November 1998	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

**Status (pending, patented,
abandoned)**

_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint:

Norman F. Oblon, Registration Number 24, 618;
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 Robert W. Hahl, Registration Number 33, 893; our (my) attorneys, with full

powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P. C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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 Post Office Address: same as residence

	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360	2361	2362	2363	2364	2365	2366	2367	2368	2369	2370	2371	2372	2373	2374	2375	2376	2377	2378	2379	2380	2381	2382	2383	2384	2385	2386	2387	2388	2389	2390	2391	2392	2393	2394	2395	2396	2397	2398	2399	2400	2401	2402	2403	2404	2405	2406	2407	2408	2409	2410	2411	2412	2413	2414	2415	2416	2417	2418	2419	2420	2421	2422	2423	2424	2425	2426	2427	2428	2429	2430	2431	2432	2
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